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Synthesis of new amino sugar derivatives from keto-sugars of D-xylose

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Abstract—Several amino sugars and imino sugar derivatives were synthesized from keto-sugars of D-xylose through a series of reactions such as the Henry reaction, hydrogenation reactions, and nucleophilic addition reactions or substitution reactions. Thiazine derivative **15** was obtained by the reaction of the keto-sugar with NH_2CSNH_2. Higher carbon sugar **16** was accidentally prepared at room temperature from the keto-sugar in the presence of NH_2CONH_2. The structures of the compounds were confirmed by spectral analysis. The absolute configurations of all asymmetric carbon atoms of **6** and **8** were confirmed by X-ray crystallographic analysis.
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Keywords: Imino sugar; Amino sugar; Thiazine; Synthesis; X-ray crystallographic analysis

1. Introduction

Carbohydrates and their derivatives are potentially useful substrates in the chemical and biological fields. To improve the function of compounds with new and attractive characteristics,[1] structural modifications can occur by substitution with nitrogen, sulfur, phosphate, or chlorine, and other groups.[2] Amino sugars are very important sugar derivatives, which are fundamental constitutents[3,4] of many biologically active compounds, such as antibiotics[5,6] and biopolymers.[7] It is known, for example, that the relative stereochemistry of the functional groups in natural and unnatural amino sugars plays an important role on the activity profile of the anthracyclines.[8] Especially heterocycles containing nitrogen or sulfur (or both) are common features incorporated in the structures of numerous natural products and pharmaceutical compounds.[9] Some imino sugars are glycosidase inhibitors with potential medicinal applications in the treatment of diabetes, obesity, and viral infections including HIV-1.[10] Due to their structural resemblance to the putative transition states[11] of the sugars involved in these processes, a variety of monocyclic[12] and bicyclic[13] imino sugars have been synthesized or isolated from natural sources over the years. Imino sugar **1** was synthesized by reduction of a nitro compound and acetylation;[14] imino sugars **2** and **3** were obtained by reduction of the corresponding cyano compounds[15] and imino sugar **4**[10] and its homologues were synthesized from other amino sugar precursors (Fig. 1).

Compounds containing thiazine, thiazoline, or/and thiazolidine rings have already been demonstrated to be antitumor, analgesic, antibiotic, antiviral, antihistaminic, anti-HIV, anti-inflammatory, and sedative agents.[16] Some thiazine derivatives were also proved to have excellent NO synthase inhibition activities.[17] The development of simple and effective methods for their preparation has aroused considerable interest in the field of medicinal chemistry.

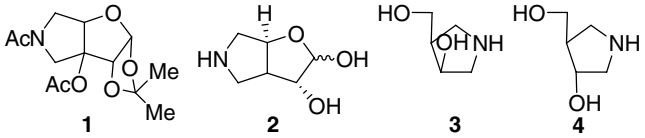

Figure 1. Examples of imino sugars.

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In this paper, several new branched-chain amino sugar derivatives and some imino sugars bearing a pyrrole ring similar to imino sugar **2** were synthesized from keto-sugars derived from D-xylose. Thiazine derivative **15** was obtained by the reaction of the 3-keto-sugar with NH_2CSNH_2, and a higher carbon sugar **16** was accidentally obtained in the presence of NH_2CONH_2 at room temperature from the 3-keto-sugar derivative of D-xylose.

2. Results and discussion

2.1. Synthetic transformations

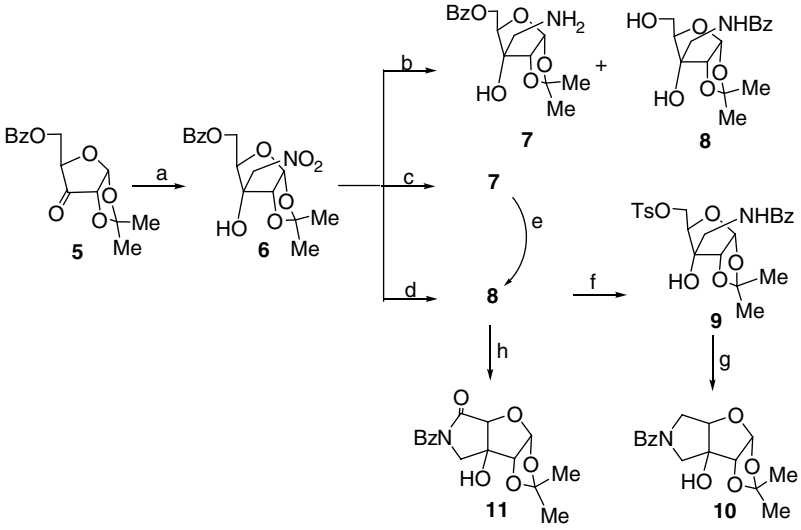
In the presence of KF, addition of nitromethane to the carbonyl group of 5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-*erythro*-ketofuranos-3-ulose (**5**), derived from D-xylose, took place stereoselectively to give only the ribo isomer **6** in almost quantitative yield (Scheme 1). KF was found to be better than any other base for this reaction. The presence of a nitro group in the structure was indicated by IR spectral analysis, and the absolute configuration of all asymmetric carbon atoms was confirmed by single-crystal X-ray crystallographic analysis (Fig. 2). The stereoselectivity probably resulted from the steric hindrance of the 1,2-*O*-isopropylidene group.

Reduction of the ribo isomer **6** with hydrogen over 10% palladium-on-charcoal under neutral conditions led to a mixture of two products. The mixture was separated by silica gel column chromatography with 1:15 MeOH–$CHCl_3$ to give the desired compound **7**, 3-*C*-aminomethyl-5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-ribofuranose, in 75% yield, plus an undesired compound **8**, 3-*C*-benzamidomethyl-1,2-*O*-isopropylidene-α-D-ribofuranose, in 10% yield. The structure of **8** was confirmed by ^1H, ^{13}C, 2D NMR, and HRMS spectra, which showed **7** and **8** to be isomers. The absolute structure of **8** was confirmed by single-crystal X-ray analysis (Fig. 2).

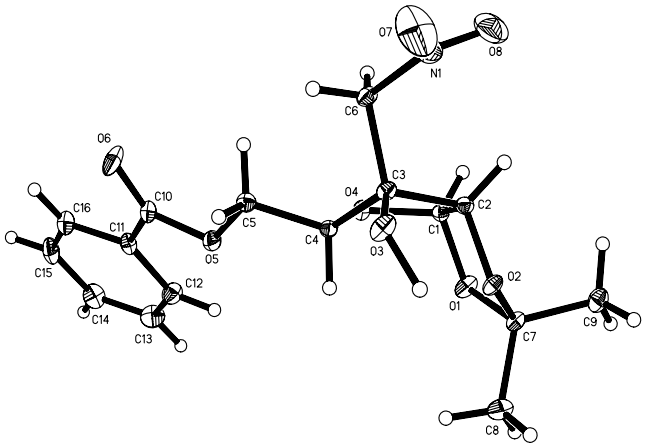
In order to control the yields of **7** and **8**, the reaction was investigated under various conditions. Prolonging the reaction time and increasing the amount of the Pd/C catalyst did not have an influence on the yields of **7** and **8**. When a catalytic amount of concentrated hydrochloric acid was dropped to the reaction mixture, compound **7** was obtained almost in quantitative yield, but compound **8** was not observed. Product **7** could be directly used in the subsequent reaction without prior purification. It was found important to control the optimum concentration range of hydrochloric acid between 0.10/100 (v/v) and 0.15/100 (v/v) to avoid the formation of other products.

It is worth noting that when the catalytic hydrogenation reaction was carried out in EtOH solution under basic conditions, product **8** was obtained almost in quantitative yield. The formation of **8** was deduced from an intramolecular transfer of the benzoyl group in **7**.[18] In order to prove this process, amino sugar **7** was refluxed in EtOH solution in the presence of Et_3N, and compound **8** was obtained in high yield.

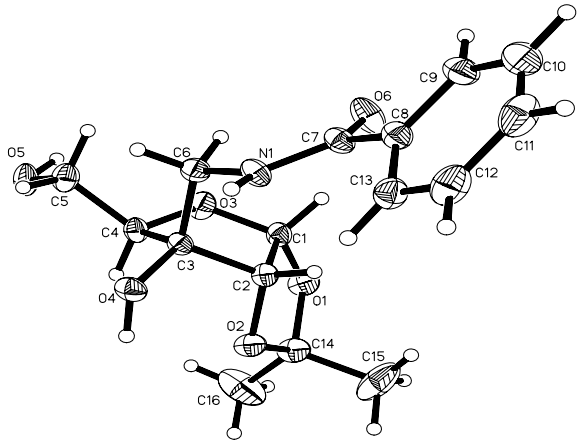
Compound **8** is a useful precursor for the synthesis of imino sugars. Sulfonylation of **8** with *p*-toluenesulfonyl chloride in anhydrous pyridine at 0 °C gave **9** in 90% yield. Treatment of **9** with NaOMe in anhydrous THF readily afforded a new imino sugar compound **10**, which is a bicyclic product containing a pyrrole ring. The NMR spectra for **10** in dimethyl sulfoxide (DMSO-d_6) at room temperature suggested the presence of two isomers. Such isomerism is due to restricted rotation about the C–N bond.[14]



Scheme 1. Reagents and conditions: (a) KF, CH_3NO_2, THF, reflux; (b) EtOH, 10% Pd/C, 50 °C, H_2 (50 psi); (c) EtOH, HCl (aq), 10% Pd/C, 50 °C, H_2 (50 psi); (d) EtOH, Et_3N, 10% Pd/C, 50 °C, H_2 (50 psi); (e) EtOH, Et_3N, reflux; (f) TsCl, pyridine, 0 °C; (g) NaOMe, THF, reflux; (h) PDC, CH_2Cl_2, reflux.



Compound **6**



Compound **8**

Figure 2. X-ray crystal structures of compounds **6** and **8**.

Oxidation of **8** with pyridinium dichromate (PDC) at reflux temperature (CH_2Cl_2) gave another bicyclic product **11** containing a pyrrole ring in 81% yield. It was likely that **8** was first oxidized to a carboxylic acid derivative, which was then transformed to lactam **11** by an intramolecular cyclization as shown in Scheme 2.

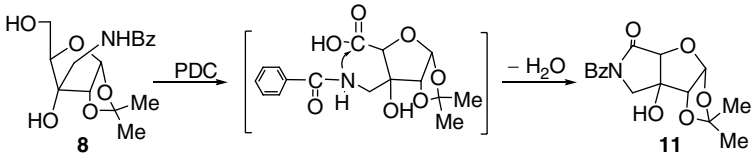
Another derivative of D-xylose, 1,2-*O*-isopropylidene-5-*O*-*p*-toluenesulfonyl-α-D-*erythro*-pentofuranos-3-ulose (**12**), was treated with nitromethane at room temperature under basic conditions to give an addition product, 1,2-*O*-isopropylidene-3-*C*-nitromethyl-5-*O*-*p*-toluenesulfonyl-α-D-ribofuranose (**13**), whose absolute structure is that of a D-ribo sugar.[14] Catalytic (10% Pd/C) hydrogenation of compound **13** under neutral conditions for 2 h gave the desired imino sugar **14**, which is a pyrrole derivative. The reduction time (2 h) was shorter than that for compound **6** (6 h), which should be a result of *p*-toluenesulfonyl group elimination and imino sugar formation.

Treatment of ulose **12** with thiourea in anhydrous THF for 4 h at 40 °C gave a new product **15** in 83% yield. The HRMS of **15** exhibited molecular ions $[M+H]^+$ at *m*/*z* 247.0760 and $[M-H]^-$ at *m*/*z* 171.0110, respectively, which showed **15** to be a *p*-toluenesulfonate salt and also indicated the loss of the tosyl group from C-5. The ^1H NMR signals for H-5 shifted upfield by 0.86 and 0.77 ppm, respectively, whereas the ^{13}C NMR signals for C-5, appearing at δ 24.3 ppm, large shifted upfield by 33.7 ppm, in comparison with the spectra for keto-sugar **12**. Only the shifts of the SCH_2 group were in agreement with the above data.[19] The HMBC spectra indicated a long-distance coupling between C=N and the C-5 proton. On the basis of the above analysis and corresponding data, the structure of **15** was confirmed to be a sugar derivative containing a thiazine ring. It is shown that this reaction is a simple method to obtain thiazine derivatives (Scheme 3).

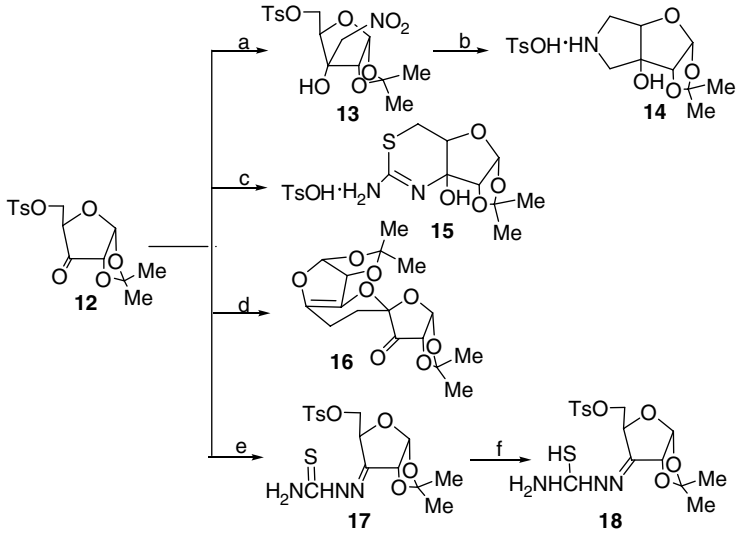
In order to get access to other similar compounds, treatment of ulose **12** with NH_2CONH_2 in anhydrous THF at room temperature for 6 h accidentally led to a higher carbon sugar **16** in 75% yield. The desired addition compound, similar to **15**, was not observed. The structure of compound **16** was confirmed from its NMR and HRMS spectra. Under basic conditions, higher carbon **16** was obtained through a hetero Diels–Alder reaction,[20] after the benzoyl group was eliminated from the 5-position to form a diene. In a previous work, compound **16** was synthesized in the presence of KF at reflux temperature. The synthesis of **16** at room temperature was first reported in the presence of NH_2CONH_2.

Similarly, treatment of **12** with $NH_2NH_2CSNH_2$, gave an amithozone **17** in 80% yield; also no imino sugar was obtained. Reduction of **17** with $NaBH_4$ gave the partially reduced product **18**, another amino sugar containing a thio atom at the branch chain.

In summary, the synthesis of new branched amino sugar derivatives, imino sugar derivatives with different functional groups and C-10 higher carbon sugar from



Scheme 2. A proposed mechanism for the formation of **11**.



Scheme 3. Reagents and conditions: (a) KF, CH_3NO_2, THF, rt; (b) EtOH, 10% Pd/C, 50 °C, H_2 (50 psi); (c) NH_2CSNH_2, THF, 40 °C; (d) NH_2CONH_2, rt, THF; (e) $NH_2NH_2CSNH_2$, THF, rt; (f) $NaBH_4$, MeOH, rt.

3-keto-D-*erythro*-pentofuranose is described. The structures of all products were confirmed by their IR, ^1H NMR, ^{13}C NMR, and HRMS spectra. These compounds could be useful in the chemical and medicinal–chemical fields. Further studies on these sugars and their derivatives are now in progress.

2.2. X-ray crystallographic analysis

Details of the crystal structure determinations for compounds **6** and **8** are summarized in Table 1. Selected torsion angles are presented in Table 2.

The X-ray crystallographic analysis proved a D-ribo configuration for compound **6**. In compound **6**, the furan ring adopts the *E* conformation. The atoms of C(1), C(2), C(3), and O(4) are coplanar. The plane equation is $-4.255x + 2.993y + 11.311z = 6.7983$, while the C(4) is away from the plane of 0.5354 Å, and the flap atom C(4) is placed in the exo direction. The substituted dioxolane ring is in the *E* conformation. The atoms of C(1), C(2), O(1), and O(2) are coplanar. The plane equation is $12.301x + -0.118y + -5.800z = 7.6908$, while the C(7) is away from the plane of 0.4051 Å and the flap atom C(7) is placed in the exo direction. The sugar plane

Table 1. Single-crystal X-ray data and structure refinement for compounds **6** and **8**

	6	**8**
Empirical formula	$C_{16}H_{19}NO_8$	$C_{16}H_{21}NO_6$
Formula weight	353.32	323.34
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	12.354	9.7016
b (Å)	5.501	12.821
c (Å)	13.514	13.439
Beta-angle	110.28(3)	90.00
V (Å^3)	861.5(3)	1671.5(6)
Z	2	4
D_{Calcd} (Mg/m^3)	1.362	1.285
Absorption coefficient (mm^{-1})	0.110	0.099
F(000)	372	688
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.18$	$0.20 \times 0.18 \times 0.17$
θ Range for data collection (°)	1.61–25.49	2.20–25.00
Index ranges	$0 \leqslant h \leqslant 14$, $-5 \leqslant k \leqslant 6$, $-16 \leqslant l \leqslant 15$	$-11 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 15$, $-15 \leqslant l \leqslant 15$
Reflections collected/unique	2175/2131 [*R*(int) = 0.1251]	5168/2761 [*R*(int) = 0.0264]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restrain/parameters	2131/1/231	2761/0/221
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0561$, $wR_2 = 0.1224$	$R_1 = 0.0330$, $wR_2 = 0.0828$
R Indices (all data)	$R_1 = 0.0704$, $wR_2 = 0.1287$	$R_1 = 0.0389$, $wR_2 = 0.0849$
Goodness-of-fit on F^2	1.011	1.032

Table 2. Selected torsion angles (°) for compounds **6** and **8**

Compound **6** angle	Deg. (°)	Compound **8** angle	Deg. (°)
C(7)–O(1)–C(1)–C(2)	−10.3(4)	C(14)–O(1)–C(1)–C(2)	10.2(2)
C(4)–O(4)–C(1)–O(1)	94.0(4)	C(4)–O(3)–C(1)–O(1)	107.70(16)
C(4)–O(4)–C(1)–C(2)	−19.5(4)	C(4)–O(3)–C(1)–C(2)	−6.82(19)
C(7)–O(2)–C(2)–C(3)	136.1(3)	C(14)–O(2)–C(2)–C(3)	138.42(17)
O(4)–C(1)–C(2)–O(2)	108.5(3)	O(3)–C(1)–C(2)–O(2)	94.93(16)
C(1)–C(2)–C(3)–C(4)	24.0(4)	C(1)–C(2)–C(3)–C(4)	35.09(17)
C(14)–C(15)–C(16)–C(11)	−0.4(8)	C(11)–C(12)–C(13)–C(8)	−1.0(3)
C(1)–O(1)–C(7)–O(2)	25.2(4)	C(1)–O(1)–C(14)–O(2)	7.3(2)
C(2)–O(2)–C(7)–O(1)	−31.0(4)	C(2)–O(2)–C(14)–O(1)	−23.2(2)
O(2)–C(2)–C(3)–C(4)	−86.9(3)	O(2)–C(2)–C(3)–C(4)	−73.98(16)
O(3)–C(3)–C(4)–C(5)	80.8(5)	O(4)–C(3)–C(4)–C(5)	76.9(2)

and the substituted dioxolane plane fused along the C(1)–C(2) bond allow the formation of a V-shaped molecule with a 75° dihedral angle.

The single-crystal X-ray diffraction analysis also reveals that there exists a kind of intermolecular hydrogen bonding interaction between O(4) and H(3A) of O(3). The neighboring molecules link to each other generating a chain via the intermolecular hydrogen bonds. Finally, the columns are bounded by the supramolecular interactions among molecules to form a regular three-dimensional network. The hydrogen-bond lengths and bond angles are listed in Table 3.

The X-ray crystallographic analysis proved a D-ribo configuration for compound **8**. Benzoyl group attachment to the N atom is in agreement with the NMR spectral analysis. In compound **8**, the furan ring also adopts the *E* conformation. Different from compound **6**, the atoms of C(1), C(2), C(4), and O(3) are coplanar in **8**. The plane equation is $6.849x + -1.643y + -9.361z = 2.9549$, while the C(3) is away from the plane of 0.6094 Å and the flap atom C(3) is placed in the exo direction. The substituted dioxolane ring adopts the *E* conformation, and the atoms of C(1), C(14), O(1), and O(2) are coplanar. The plane equation is $3.162x + -2.306y + 12.473z = 6.1738$, while the C(2) is away from the plane of −0.4059 Å and the flap atom C(2) is placed in the endo direction. The sugar plane and the substituted dioxolane plane fused along the C(1)–C(2) bond allow the formation of a V-shaped molecule with a 66.8° dihedral angle.

Different to **6**, compound **8** makes contacts with three neighboring molecules through N(1)–H(1E)···O(1), O(4)–H(4E)···O(5), and O(5)–H(5E)···O(6), respectively, which results in a reticular molecular packing. The hydrogen-bond lengths and bond angles for compounds **6** and **8** are listed in Table 3.

3. Experimental

3.1. General procedures

Melting points were measured on a WC-1 melting-point apparatus and are uncorrected. Infrared spectra were recorded using KBr discs on a Bruker Vector-22 FTIR spectrometer. Optical rotations were measured on a Perkin–Elmer 341 polarimeter. HRMS (high-resolution mass spectra) were taken with a Q-Tof Micromass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance DPX-400 spectrometer at 25 °C. The ^{1}H NMR and ^{13}C NMR chemical shifts (δ), given in parts per million, were referenced to the tetramethylsilane (TMS) signal. Coupling constants (J) are given in hertz (Hz). Thin-layer chromatography (TLC) was performed on glass plates precoated with silica gel (5–40 μm, Qingdao Marine Chemical Factory (China)) to monitor the reactions, and 10% Pd/C was purchased from Shanghai Chemical Factory (China).

3.2. X-ray diffraction experiment

X-ray diffraction analysis was carried out on a Rigaku RAXIS-IV imaging plate with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). An ortho-

Table 3. Hydrogen bonds for compounds **6** and **8**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry code
6					
O(3)–H(3A)···O(4)	1.12(8)	1.72(8)	2.820(4)	165(6)	$x, y+1, z$
8					
N(1)–H(1E)···O(1)	0.90(2)	2.07(2)	2.948(2)	165.6(19)	$-x+2, y-1/2, -z+1/2$
O(4)–H(4E)···O(5)	0.89(3)	1.93(3)	2.760(2)	155(3)	$x-1/2, -y+1/2, -z+1$
O(5)–H(5E)···O(6)	0.85(3)	1.92(3)	2.732(2)	161(3)	$-x+5/2, -y+1, z+1/2$

rhombic crystal and a monoclinic crystal were selected and mounted on a glass fiber, respectively. All data were collected at a temperature of 291(2) K and collected for Lorentz polarization effects. The structure was solved via direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydroxyl hydrogen atoms were refined with isotropic thermal parameters. Other hydrogen atoms were included but not refined. All calculations were performed using the SHELX-97 crystallographic software package.[21] Atomic coordinates and equivalent isotropic displacement parameters for compounds **6** and **8** are presented in Table 1.

3.3. 5-*O*-Benzoyl-1,2-*O*-isopropylidene-3-*C*-nitromethyl-α-D-ribofuranose (6)

To a solution of compound **5** (500 mg, 1.71 mmol) in anhyd THF (15 mL) was added CH_3NO_2 (2 mL, 37.1 mmol) and KF (125 mg, 2.1 mmol). The mixture was refluxed for 50 min and evaporated in vacuum to dryness. The residue was treated with EtOAc (100 mL) and water (50 mL), the organic phase was separated, and the aq phase was extracted with EtOAc (2 × 50 mL). The combined organics were washed with satd aq NaCl (2 × 15 mL), H_2O (2 × 15 mL) dried over anhyd Na_2SO_4. Filtration, evaporation, and crystallization of the crude product from MeOH gave compound **6** as a white solid (575 mg, 95%): mp 159.5–161.0 °C, $[\alpha]_D^{20}$ +12.3 (*c* 0.64, EtOAc); R_f 0.85 (7:3 $CHCl_3$–EtOAc); IR (KBr): 3397, 1726, 1553, 1281, 1007 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.41 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 4.26 (dd, 1H, $J_{4,5b}$ 4.4, $J_{4,5a}$ 6.0 Hz, H-4), 4.44 (dd, 1H, $J_{4,5a}$ 6.0, $J_{5a,5b}$ 12.0 Hz, H-5a), 4.52 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.63 (dd, 1H, $J_{4,5b}$ 4.4, $J_{5a,5b}$ 12.0 Hz, H-5b), 4.81 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6b), 4.91 (d, 1H, $J_{2,1}$ 4.0 Hz, H-2), 5.95 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 7.44–8.05 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$): δ 26.2 (CH_3), 26.5 (CH_3), 60.5 (C-5), 76.2 (CH_2NO_2), 78.2 (C-3), 78.7 (C-4), 79.2 (C-2), 103.5 (C-1), 113.4 ($C(CH_3)_2$), 128.5 (Ar–C), 129.1 (Ar–C), 129.7 (Ar–C), 133.4 (Ar–C), 165.9 (C=O); HRMS: calcd for $[M+Na]^+$: *m*/*z* 376.1008; found: *m*/*z* 376.1018.

3.4. 3-*C*-Aminomethyl-5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-ribofuranose (7)

(1) To a solution of compound **6** (500 mg, 1.42 mmol) in EtOH (80 mL) was added 10% Pd/C (200 mg) and 0.1 mL 37% aq HCl. The mixture was hydrogenated at 50 °C under 50 psi for 5 h. The resulting mixture was filtered and concentrated under reduced pressure to dryness, followed by crystallization from EtOAc, affording compound **7** as a white solid (425 mg, 93%): mp 163.2–164.4 °C; $[\alpha]_D^{20}$ +16.5 (*c* 0.73, MeOH); R_f 0.40 (1:5 MeOH–$CHCl_3$); IR (KBr): 3457, 2982, 1707, 1214, 1112, 1007 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.29 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.92 (d, 1H, $J_{6a,6b}$ 13.2 Hz, H-6a), 3.01 (d, 1H, $J_{6a,6b}$ 13.2 Hz, H-6b), 4.22 (dd, 1H, $J_{4,5b}$ 3.0, $J_{4,5a}$ 6.9 Hz, H-4), 4.35 (dd, 1H, $J_{5a,4}$ 7.0, $J_{5a,5b}$ 12.1 Hz, H-5a), 4.60 (dd, 1H, $J_{4,5b}$ 3.0, $J_{5a,5b}$ 12.0 Hz, H-5b), 4.76 (d, 1H, $J_{1,2}$ 3.4 Hz, H-2), 5.81 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 6.04 (s, 1H, OH-H), 7.54–7.99 (m, 5H, Ar–H), 8.25 (s, 2H, NH_2–H); ^{13}C NMR (DMSO-d_6): δ 26.2 (CH_3), 26.3 (CH_3), 39.8 (C-6), 61.5 (C-5), 77.2 (C-3), 77.7 (C-4), 78.9 (C-2), 102.9 (C-1), 111.6 ($CH(CH_3)_2$), 128.8 (Ar–C), 129.2 (Ar–C), 133.5 (Ar–C), 165.3 (C=O); HRMS: calcd for $[M+H]^+$: *m*/*z* 324.1447; found: *m*/*z* 324.1441.

(2) To a solution of compound **6** (500 mg, 1.42 mmol) in EtOH (80 mL) was added 10% Pd/C (200 mg). The mixture was hydrogenated at 50 °C under 50 psi for 6 h. The resulting mixture was filtered and concentrated under reduced pressure to dryness, and the crude product was purified by chromatography on silica gel with 1:15 MeOH–$CHCl_3$ to give **7** (345 mg, 75%) and **8** (46 mg, 10%), respectively.

3.5. 3-*C*-Benzamidomethyl-1,2-*O*-isopropylidene-α-D-ribofuranose (8)

(1) To a solution of compound **6** (500 mg, 1.42 mmol) in EtOH (80 mL) was added 10% Pd/C (200 mg) and Et_3N (3 mL). The mixture was hydrogenated at 50 °C under 50 psi for 5 h. The resulting mixture was filtered and concentrated under reduced pressure to dryness, followed by crystallization from EtOH, affording compound **8** as a white solid (413 mg, 91%): mp 189.1–190.2 °C; $[\alpha]_D^{20}$ +55.0 (*c* 0.78, MeOH); R_f 0.60 (1:5 MeOH–$CHCl_3$); IR (KBr): 3377, 3337, 1650, 1551, 1073, 1032 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.23 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 3.22 (dd, 1H, $J_{6a,NH}$ 5.3, $J_{6a,6b}$ 14.0 Hz, H-6a), 3.46 (dd, 1H, $J_{6b,NH}$ 6.9, $J_{6a,6b}$ 13.9 Hz, H-6b), 3.56 (m, 1H, H-5), 3.63 (m, 1H, H-5), 3.89 (dd, 1H, $J_{4,5a}$ 2.3, $J_{4,5b}$ 7.2 Hz, H-4), 4.26 (d, 1H, $J_{2,1}$ 3.7 Hz, H-2), 4.88 (t, 1H, *J* 5.4 Hz, OH-5), 5.24 (s, 1H, OH-3), 5.70 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 7.46–7.88 (m, 5H, Ar–H), 8.41 (t, 1H, *J* 6.0 Hz, NH); ^{13}C NMR (DMSO-d_6): δ 26.6 (CH_3), 26.9 (CH_3), 41.4 (C-6), 59.0 (C-5), 79.8 (C-3), 80.8 (C-2), 82.1 (C-4), 103.5 (C-1), 111.4 ($C(CH_3)_2$), 127.6 (Ar–C), 128.7 (Ar–C), 131.7 (Ar–C), 134.3 (Ar–C), 167.4 (C=O); HRMS: calcd for $[M+Na]^+$: *m*/*z* 346.1267; found: *m*/*z* 346.1270.

(2) To a solution of compound **7** (500 mg, 1.5 mmol) in anhyd MeOH (10 mL) was added Et_3N (0.5 mL). The mixture was refluxed for 3 h, evaporated in vacuum, and crystallized from EtOH to give compound **8** as a white solid (412 mg, 90%).

3.6. 3-*C*-Benzamidomethyl-1,2-*O*-isopropylidene-5-*O*-*p*-toluenesulfonyl-α-D-ribofuranose (9)

To a solution of compound **8** (500 mg, 1.5 mmol) in anhyd pyridine (20 mL) was added *p*-toluenesulfonyl chloride (342 mg, 1.8 mmol) at 0 °C. The mixture was stirred for 24 h at 0 °C, poured into 50 mL of ice-water, and extracted with EtOAc (2 × 50 mL). The combined organics were washed with satd aq NaCl (2 × 15 mL), H_2O (2 × 15 mL), dried over anhyd Na_2SO_4, then filtered, evaporated, and crystallized from MeOH to give compound **9** as a white solid (665 mg, 90%): mp 144.6–146.1 °C; $[\alpha]_D^{20}$ +32.2 (*c* 0.53, EtOAc); R_f 0.7 (7:3 $CHCl_3$–EtOAc); IR (KBr) 3449, 1647, 1530, 1362, 1173 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.31 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.32 (dd, 1H, $J_{6a,NH}$ 4.4, $J_{6a,6b}$ 14.0 Hz, H-6a), 3.79 (dd, 1H, $J_{6b,NH}$ 8.0, $J_{6a,6b}$ 14.0 Hz, H-6b), 4.02 (dd, 1H, $J_{4,5b}$ 3.2, $J_{4,5a}$ 6.8 Hz, H-4), 4.14 (dd, 1H, $J_{5a,4}$ 6.8, $J_{5a,5b}$ 10.8 Hz, H-5a), 4.29 (d, 1H, $J_{2,1}$ 3.6 Hz, H-2), 4.37 (dd, 1H, $J_{5b,4}$ 3.2, $J_{5a,5b}$ 10.8 Hz, H-5b), 5.81 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 6.66 (m, 1H, NHCO), 7.33–7.80 (m, 9H, Ar–H); ^{13}C NMR ($CDCl_3$): δ 21.7 (CH_3), 26.4 (CH_3), 26.5 (CH_3), 40.0 (C-6), 66.6 (C-5), 78.8 (C-4), 79.6 (C-3), 79.7 (C-2), 103.7 (C-1), 112.9 ($CH(CH_3)_2$), 127.0 (Ar–C), 128.1 (Ar–C), 128.7 (Ar–C), 130.0 (Ar–C), 132.0 (Ar–C), 132.3 (Ar–C), 133.6 (Ar–C), 145.2 (Ar–C), 167.9 (C=O); HRMS: calcd for $[M+Na]^+$: *m*/*z* 500.1355; found: *m*/*z* 500.1361.

3.7. *N*-Benzoyl-5-deoxy-3,5-imino-1,2-*O*-isopropylidene-α-D-ribofuranose (10)

To a solution of compound **9** (500 mg, 1.04 mmol) in anhyd THF (20 mL) was added NaOMe (0.5 mL). The mixture was refluxed for 5 h, and then evaporated in vacuum. The residue was dissolved in water, extracted with EtOAc, and the organic layer was dried over Na_2SO_4, and then filtered, evaporated, and crystallized from MeOH to give compound **10** as a white solid (273 mg, 86%): mp 203.2–203.8 °C; $[\alpha]_D^{20}$ +145.7 (*c* 0.74, $CHCl_3$); R_f 0.4 (7:3 $CHCl_3$–EtOAc); IR (KBr) 3170, 1606, 1593, 1572, 1459, 1438, 1067 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.26 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.34 (m, 1H, H-6), 3.43 (d, 1H, *J* 12.4 Hz, H-5), 3.53 (d, 3H, *J* 12.4 Hz, H-6), 3.65 (t, 1H, *J* 13.8 Hz, H-5), 3.73 (m, 2H, H-5), 4.23 (d, 1H, *J* 2.9 Hz, H-4), 4.32 (d, 1H, *J* 3.4 Hz, H-4), 4.38 (d, 1H, *J* 3.6 Hz, H-2), 4.54 (d, 1H, *J* 3.6 Hz, H-2), 5.58 (s, 1H, OH-3), 5.63 (s, 1H, OH-3), 5.84 (d, 1H, *J* 3.6 Hz, H-1), 5.86 (d, 1H, *J* 3.6 Hz, H-1), 7.42–7.51 (m, 10H, Ar–H); ^{13}C NMR (DMSO-d_6): δ 26.7 (CH_3), 27.0 (CH_3), 50.3 (C-5), 52.9 (C-5), 55.1 (C-6), 57.2 (C-6), 80.1 (C-2), 80.7 (C-2), 81.2 (C-4), 82.6 (C-4), 83.9 (C-3), 85.7 (C-3), 105.2 (C-1), 111.9 ($CH(CH_3)_2$), 112.0 ($CH(CH_3)_2$), 127.3 (Ar–C), 128.5 (Ar–C), 128.5 (Ar–C), 130.2 (Ar–C), 136.4 (Ar–C), 136.6 (Ar–C), 169.0 (C=O); HRMS: calcd for $[M+Na]^+$: *m*/*z* 328.1161; found: *m*/*z* 328.1165.

3.8. 3-*C*-Benzamidomethyl-1,2-*O*-isopropylidene-α-D-ribofuranosonic acid 3,5-lactam (11)

To a solution of compound **8** (400 mg, 1.2 mmol) in anhyd CH_2Cl_2 (20 mL) was added pyridinium dichromate (PDC, 300 mg). The mixture was heated at reflux for 3 h, and then evaporated in vacuum. The residue was dissolved in EtOAc and filtered through silica gel G. The EtOAc layer was dried over Na_2SO_4, filtered, and evaporated, and the crude product was crystallized from MeOH to give compound **11** as a white solid (320 mg, 81%): mp 162.5–165.4 °C; $[\alpha]_D^{20}$ +155.6 (*c* 0.64, EtOAc); R_f 0.6 (7:3 $CHCl_3$–EtOAc); IR (KBr) 3455, 1763, 1676, 1321 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.44 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 3.92 (d, 1H, $J_{6a,6b}$ 12.8 Hz, H-6a), 4.19 (d, 1H, $J_{6a,6b}$ 12.8 Hz, H-6b), 4.37 (s, 1H, H-4), 4.53 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 6.06 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 7.43–7.65 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$): δ 26.9 (CH_3), 27.1 (CH_3), 53.6 (C-6), 78.8 (C-3), 81.5 (C-4), 84.7 (C-2), 107.1 (C-1), 114.5 ($CH(CH_3)_2$), 128.0 (Ar–C), 129.1 (Ar–C), 132.5 (Ar–C), 133.4 (Ar–C), 167.8 (C=O), 170.3 (C=O); HRMS: calcd for $[M+Na+MeOH]^+$: *m*/*z* 374.1216; found: *m*/*z* 374.1212.

3.9. 1,2-*O*-Isopropylidene-3-*C*-nitromethyl-5-*O*-*p*-toluenesulfonyl-α-D-ribofuranose (13)

To a solution of compound **12** (500 mg, 1.46 mmol) in anhyd THF (15 mL) was added CH_3NO_2 (2 mL, 37.1 mmol) and KF (125 mg, 2.1 mmol). The mixture was stirred at room temperature for 6 h and then evaporated in vacuum to dryness. The residue was treated with EtOAc (100 mL) and water (50 mL), the organic phase was separated, and the aq phase was extracted with EtOAc (2 × 50 mL). The combined organics were dried over anhyd Na_2SO_4, filtered, evaporated, and crystallized from MeOH to afford compound **13** as a white solid (536 mg, 91%): mp 133.0–134.0 °C, lit.[14] 131.5–132 °C; $[\alpha]_D^{20}$ +23.7 (*c* 0.65, EtOAc); R_f 0.85 (7:3 $CHCl_3$–EtOAc); IR (KBr): 3462, 1555, 1364, 1174, 1101, 992 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.38 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 4.06 (t, 1H, $J_{4,5a}$ 4.0 Hz, H-4), 4.18 (dd, 1H, $J_{5a,4}$ 4.8, $J_{5a,5b}$ 11.2 Hz, H-5a), 4.30 (dd, 1H, $J_{5a,5b}$ 11.2, $J_{5b,4}$ 3.2 Hz, H-5b), 4.40 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.62 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6b), 4.82 (d, 1H, $J_{2,1}$ 4.0 Hz, H-2), 5.85 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 7.36–7.81 (m, 4H, Ar–H); ^{13}C NMR ($CDCl_3$): δ 21.7 (CH_3), 26.2 (CH_3), 26.5 (CH_3), 65.3 (C-5), 76.3 (C-6), 78.0 (C-3), 78.9 (C-4), 79.3 (C-2), 103.5 (C-1), 113.6 ($C(CH_3)_2$), 128.1 (Ar–C), 130.1 (Ar–C), 132.1 (Ar–C), 145.5 (Ar–C); HRMS: calcd for $[M+Na]^+$: *m*/*z* 426.0835; found: *m*/*z*

426.0822; calcd for $[M+K]^+$: m/z 442.0574; found: m/z 442.0569.

3.10. 5-Deoxy-3,5-imino-1,2-*O*-isopropylidene-α-D-ribofuranose, *p*-toluenesulfonate salt (14)

To a solution of compound **13** (500 mg, 1.2 mmol) in MeOH (80 mL) was added 10% Pd/C (200 mg). The mixture was hydrogenated at 50 °C under 50 psi for 2 h. The resulting mixture was filtered and concentrated under reduced pressure to dryness, followed by crystallization from MeOH, affording compound **14** as a white solid (415 mg, 89%): mp 190.7–192.8 °C; $[\alpha]_D^{20}$ +36.3 (*c* 0.73, MeOH); R_f 0.40 (1:3 MeOH–$CHCl_3$); IR (KBr): 3367, 2979, 1617, 1195, 1175, 1081, 1011 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.29 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.34 (m, 2H, H-6), 3.38 (m, 2H, H-5), 4.38 (d, 1H, $J_{4,5}$ 2.8 Hz, H-4), 4.56 (d, 1H, $J_{2,1}$ 3.6 Hz, H-2), 5.85 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 5.97 (s, 1H, OH-3), 7.11–7.50 (m, 4H, Ar–H), 9.30 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6): δ 21.0 (CH_3), 26.7 (CH_3), 26.9 (CH_3), 49.1 (C-5), 52.8 (C-6), 80.0 (C-2), 82.6 (C-4), 86.3 (C-3), 105.2 (C-1), 112.4 ($C(CH_3)_2$), 125.7 (Ar–C), 128.3 (Ar–C), 137.9 (Ar–C), 145.7 (Ar–C); HRMS: calcd for $[M+H]^+$: m/z 202.1079; found: m/z 202.1079; calcd for $[M-H]^-$: m/z 171.0116; found: m/z 171.0119.

3.11. (3a*R*,4a*S*,8a*S*,8b*R*)-7-amino-2,2-dimethyl-3a,4a,5,8b-tetrahydro-8a*H*-[1,3]dioxolo[4,5]furo[3,2-*d*][1,3]thiazin-8a-ol (15)

To a solution of compound **12** (500 mg, 1.46 mmol) in THF (20 mL) was added NH_2CSNH_2 (122 mg, 1.60 mmol). The mixture was heated at 40 °C for 4 h, then evaporated to dryness. The crude product was crystallized from EtOAc to give compound **15** as a white solid (350 mg, 83%): mp 190.5–191.6 °C; $[\alpha]_D^{20}$ −64.9 (*c* 1.0, MeOH); R_f 0.40 (1:5 MeOH–$CHCl_3$); IR (KBr): 3303, 1654, 1614, 1486, 1216, 1090 cm^{-1}; ^1H NMR (D_2O): δ 1.34 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.40 (dd, 1H, $J_{5a,4}$ 3.9, $J_{5a,5b}$ 14.6 Hz, H-5a), 3.52 (d, 1H, $J_{5a,5b}$ 14.6 Hz, H-5b), 4.52 (m, 1H, H-4), 4.60 (d, 1H, $J_{2,1}$ 3.6 Hz, H-2), 5.88 (d, 1H, $J_{2,1}$ 3.6 Hz, H-1), 7.30–7.63 (m, 4H, Ar–H); ^{13}C NMR (D_2O): δ 20.9 (CH_3), 24.3 (C-5), 25.9 (CH_3), 26.0 (CH_3), 70.0 (C-4), 82.2 (C-2), 86.1 (C-3), 104.0 (C-1), 115.4 ($C(CH_3)_2$), 125.8 (Ar–C), 129.9 (Ar–C), 139.9 (Ar–C), 142.9 (Ar–C), 168.0 (C=N); HRMS: calcd for $[M+H]^+$: 247.0753; found: 247.0760; calcd for $[M-H]^-$: 171.0116; found: 171.0110.

3.12. Carbon-10 higher carbon compound (16)

To a solution of compound **12** (500 mg, 1.46 mmol) in THF (20 mL) was added NH_2CONH_2 (96 mg, 1.60 mmol). The mixture was stirred at room temperature for 6 h and evaporated to dryness. The residue was dissolved in water (50 mL), extracted with EtOAc (2 × 50 mL), and the combined organics were dried over anhyd Na_2SO_4, filtered, and evaporated. The crude product was crystallized from Et_2O to afford compound **16** as a white solid (371 mg, 75%): mp 166.1–168.0 °C; $[\alpha]_D^{20}$ +49.1 (*c* 0.20, $CHCl_3$); R_f 0.60 (7:3 $CHCl_3$–EtOAc); IR (KBr): 3440, 2990, 1794, 1634, 1214, 1090 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.35 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.93 (m, 1H, H-5a), 2.03 (m, 1H, H-5b), 2.27 (m, 1H, H-6a), 2.34 (m, 1H, H-6b), 5.10 (d, 1H, $J_{1,2}$ 4.4 Hz, H-2), 5.22 (d, 1H, $J_{9,10}$ 5.2 Hz, H-9), 5.99 (d, 1H, $J_{10,9}$ 5.2 Hz, H-10), 6.10 (d, 1H, $J_{1,2}$ 4.4 Hz, H-1), ^{13}C NMR (DMSO-d_6): δ 17.1 (C-6), 25.4 (C-5), 27.1 (CH_3), 27.4 (CH_3), 27.5 (CH_3), 27.9 (CH_3), 76.0 (C-2), 79.9 (C-9), 99.9 (C-4), 101.9 (C-1), 103.6 (C-10), 112.1 (C-11), 115.4 (C-14), 129.6 (C-8), 137.3 (C-7), 202.5 (C-3); HRMS: calcd for $[M+Na+MeOH]^+$: m/z 395.1318; found: m/z 395.1321.

3.13. 1,2-*O*-Isopropylidene-5-*O*-*p*-toluenesulfonyl-α-D-*erythro*-ketofuranose-3-ulose 3-thiosemicarbazone (17)

To a solution of compound **12** (500 mg, 1.46 mmol) in THF (20 mL) was added $NH_2NH_2CSNH_2$ (145 mg, 1.60 mmol). The mixture was stirred at room temperature for 5 h, and evaporated to dryness. The residue was treated with EtOAc (100 mL) and water (50 mL), the organic phase was separated, and the aq phase was extracted with EtOAc (2 × 50 mL). The combined organics were dried over anhyd Na_2SO_4, filtered, and evaporated. The residue was purified by chromatography (9:1 $CHCl_3$–EtOAc) to give compound **17** as a syrup (511 mg, 80%): $[\alpha]_D^{20}$ +220.0 (*c* 0.75, $CHCl_3$); R_f 0.6 (1:1 EtOAc–petroleum ether); IR (KBr): 3338, 1598, 1494, 1359, 1176, 1065 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.42 (s, 6H, $2CH_3$), 2.47 (s, 3H, CH_3), 4.25 (dd, 1H, $J_{5a,4}$ 2.6, $J_{5a,5b}$ 10.8 Hz, H-5a), 4.31 (dd, 1H, $J_{5b,4}$ 2.4, $J_{5a,5b}$ 10.8 Hz, H-5b), 4.86 (m, 1H, H-4), 5.00 (d, 1H, $J_{1,2}$ 4.6 Hz, H-2), 5.96 (d, 1H, $J_{1,2}$ 4.6 Hz, H-1), 6.49 (s, 1H, NH_2), 7.10 (s, 1H, NH_2), 7.27–7.75 (m, 4H, Ar–H), 9.20 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 21.7 (CH_3), 27.2 (CH_3), 27.4 (CH_3), 69.3 (C-5), 74.2 (C-2), 76.8 (C-4), 104.8 (C-1), 114.6 ($C(CH_3)_2$), 127.8 (Ar–C), 130.1 (Ar–C), 132.4 (Ar–C), 145.5 (Ar–C), 150.3 (C-3), 179.6 (C=S); HRMS: calcd for $[M+Na]^+$: m/z 438.0769; found: m/z 438.0758.

3.14. 1,2-*O*-Isopropylidene-5-*O*-*p*-toluenesulfonyl-α-D-*erythro*-ketofuranose-3-ulose 3-hydrothiosemicarbazone (18)

To a solution of compound **17** (500 mg, 1.20 mmol) in anhyd MeOH (20 mL) was added $NaBH_4$ (70 mg,

1.81 mmol). The mixture was stirred at room temperature for 5 h, and then concentrated. The crude product was submitted to silica gel column chromatography (1:1 $CHCl_3$–EtOAc) to afford compound **18** as a white solid (392 mg, 78%): mp 125.0–126.1 °C, $[\alpha]_D^{20}$ +96.6 (*c* 0.45, $CHCl_3$); R_f 0.6 (7:3 $CHCl_3$–EtOAc); IR (KBr): 3346, 1596, 1360, 1190, 1175 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.36 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 3.39 (dd, 1H, *J* 4.0 Hz, H-CHS), 3.89 (m, 1H, H-4), 4.22 (dd, 1H, $J_{5a,4}$ 2.7, $J_{5a,5b}$ 11.2 Hz, H-5a), 4.32 (dd, 1H, $J_{5b,4}$ 3.1, $J_{5a,5b}$ 11.3 Hz, H-5b), 4.50 (s, 1H, SH) 4.74 (t, 1H, $J_{1,2}$ 3.6 Hz, H-2), 5.77 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 6.45 (s, 1H, NH_2), 7.24 (s, 1H, NH), 7.28–7.80 (m, 4H, Ar–H), 7.97 (s, 1H, NH_2); ^{13}C NMR ($CDCl_3$): δ 21.7 (CH_3), 26.3 (CH_3), 26.5 (CH_3), 63.0 (C-S), 67.5 (C-5), 75.0 (C-4), 77.2 (C-2), 104.6 (C-1), 113.1 ($C(CH_3)_2$), 128.0 (Ar–C), 130.1 (Ar–C), 130.1 (C-3), 132.3 (Ar–C), 145.5 (Ar–C); HRMS: calcd for $[M+Na]^+$: *m*/*z* 440.0927; found: *m*/*z* 440.0912.

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Supplementary data

Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 604081 (**6**) and CCDC No. 604082 (**8**). Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). NMR and mass spectra have been included in the Supplementary data section of the electronic version of this paper and can be accessed at doi:10.1016/j.carres.2006.06.018.

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